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Protection of Advanced Copper Alloys With Lean Cu-Cr Coatings

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Abstract

Advanced copper alloys are used as liners of rocket thrusters and nozzle ramps to ensure dissipation of the high thermal load generated during launch, and Cr-lean coatings are preferred for the protection of these liners from the aggressive ambient environment. It is shown that adequate protection can be achieved with thin Cu-Cr coatings containing as little as 17% Cr.

Introduction

The excellent thermal conductivity of copper alloys makes them preferred liner materials for rocket engine combustors and nozzle ramps, where dissipation of a huge thermal load is important. Pure Cu has a thermal conductivity of 300 W/mK (at 20 °C), the highest for any material; and comparable values for the advanced Cu alloys being considered for liner application (CuCrNb, CuAgZr, and ODS Cu-Al₂O₃) are 300 to 360 W/mK [3], representing a low-to-moderate 6 to 23% drop from Cu. However, the poor resistance of Cu and its alloys to oxidative degradation needs to be overcome. One solution is the development of special copper alloys with better oxidation resistance, a good example being Cu-8Cr-4Nb [1,2]. Another is the use of an environmental-barrier coating, provided the coating material does not seriously impair thermal conductivity (and ductility) of the liner alloy.

Cu-Cr coatings are favored because they can provide a protective Cr₂O₃ scale upon oxidation, while maintaining good chemical match as well as acceptable thermal match with a Cu-alloy substrate. Ken Chiang and his co-workers have demonstrated the formation of a continuous Cr₂O₃ sub-layer from Cu-30vol%Cr coatings on Cu alloys [4–6]. NiCrAlY is another candidate coating material. Though its intrinsic thermal conductivity is lower than that of Cu-Cr compositions, it enables liner service at higher wall temperatures, while its preferential oxidation to Al₂O₃ (when its Al content exceeds ~5%) yields an even more protective oxide scale.

Our aim was to develop Cu-Cr coatings to protect Cu alloys via adequate formation of Cr₂O₃, while keeping Cr content low enough so as not to impair ductility or thermal conductivity of the system. A rough, rule-of-mixtures estimation shows that thermal conductivity of a Cu-30%Cr composition should be ~240 W/mK, only 60% of the value for pure Cu, and 20 to 35% below the values given above for candidate liner alloys. It is important to reduce this deficit of thermal conductivity by reducing its Cr content while preserving its ability to provide Cr₂O₃ cover.

A straight-forward way to do it is to make the coating fine-textured and homogeneous. The coatings studied by Chiang et al. were rather coarse aggregates of Cu and Cr particles. Of course, oxidation would yield Cr₂O₃ islands which conform to the same texture but coalesce eventually

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into a continuous Cr_2O_3 layer. That is perhaps why they needed 30% and higher Cr levels to achieve protection. Advanced coating techniques now enable the routine deposition of coatings with fine microstructures. Accordingly, one goal of this work was to demonstrate that Cr-lean coatings can be put down on Cu alloys from powder, using plasma spray or cold spray.

Experimental Details

The coating compositions used in our study were Cu-8.5Cr, Cu-17.1Cr, Cu-21.3Cr, and Cu-25.6 Cr (Cr content in wt%). They were deposited from corresponding powders by low-pressure-plasma spray (LPPS) or by a variant of cold-spray called “kinetic metallization” (KM). The powders, –635 mesh ($<15\text{ }\mu\text{m}$ average particle size) were made by *Crucible Research* of Pittsburgh, PA with O_2 contents ranging from 425 ppm by wt. (wppm) for Cu-8.5Cr to 650 wppm for Cu-25.6Cr. KM deposition was by *Inovati* of Santa Barbara, CA, and LPPS was done in-house. The substrates were polished coupons (19 mm in diameter, 1.0 mm thick). Consolidation of the coatings was done by post-anneal or by HIPing (100 MPa) in Ar at 930 °C. Static oxidation test was done in a thermo-gravimetric analyzer (TGA) in 2.2 vol% O_2 (bal Ar), while cyclic oxidation was by TGA in air. This choice of low- $p(\text{O}_2)$ ambient was based on a typical thrust-cell environment [8]. Rods of the same Cu-Cr compositions made by KM were cut into mini-disks 5 to 7 mm in diameter for oxidation-reduction studies, polished to a mirror finish, and subjected to *in-situ* cycles of oxidation-reduction (air-to- H_2/Ar). Details of this novel test are given in a companion paper [7].

Results and Discussion

Results presented here for coatings on Cu-8Cr-4Nb were similar to those obtained with corresponding coating on Cu-3Ag-0.5Zr (the current Space Shuttle Main Engine liner). So, substrate details did not affect the results. LPPS coatings were brownish due to oxygen pick-up, and turned black upon anneal as the oxygen was incorporated into oxide. In contrast, KM coatings retained their color and luster through deposition and anneal, indicating they were significantly oxygen-free. Accordingly, the rest of this paper considers only the KM coatings. (LPPS coatings were mentioned just to highlight an advantage of cold deposition for Cu alloys.)

Figure 1 shows a KM-coated sample after 10 hr oxidation at 650 °C. In (A) a Cu-25.6Cr coating with an oxide skin (to the right) lies on the featureless substrate (to the left). Details of the coating appear in (B): dark Cr lumps within the lighter Cu matrix; (C) and (D) are corresponding EDS spectra.

Static Oxidation

Figure 2 presents histograms of the static oxidation weight gains in 2.2% O_2 at various temperatures, and a kinetic plot comparing 650 °C weight gain rates for the bare substrate and a coated substrate.

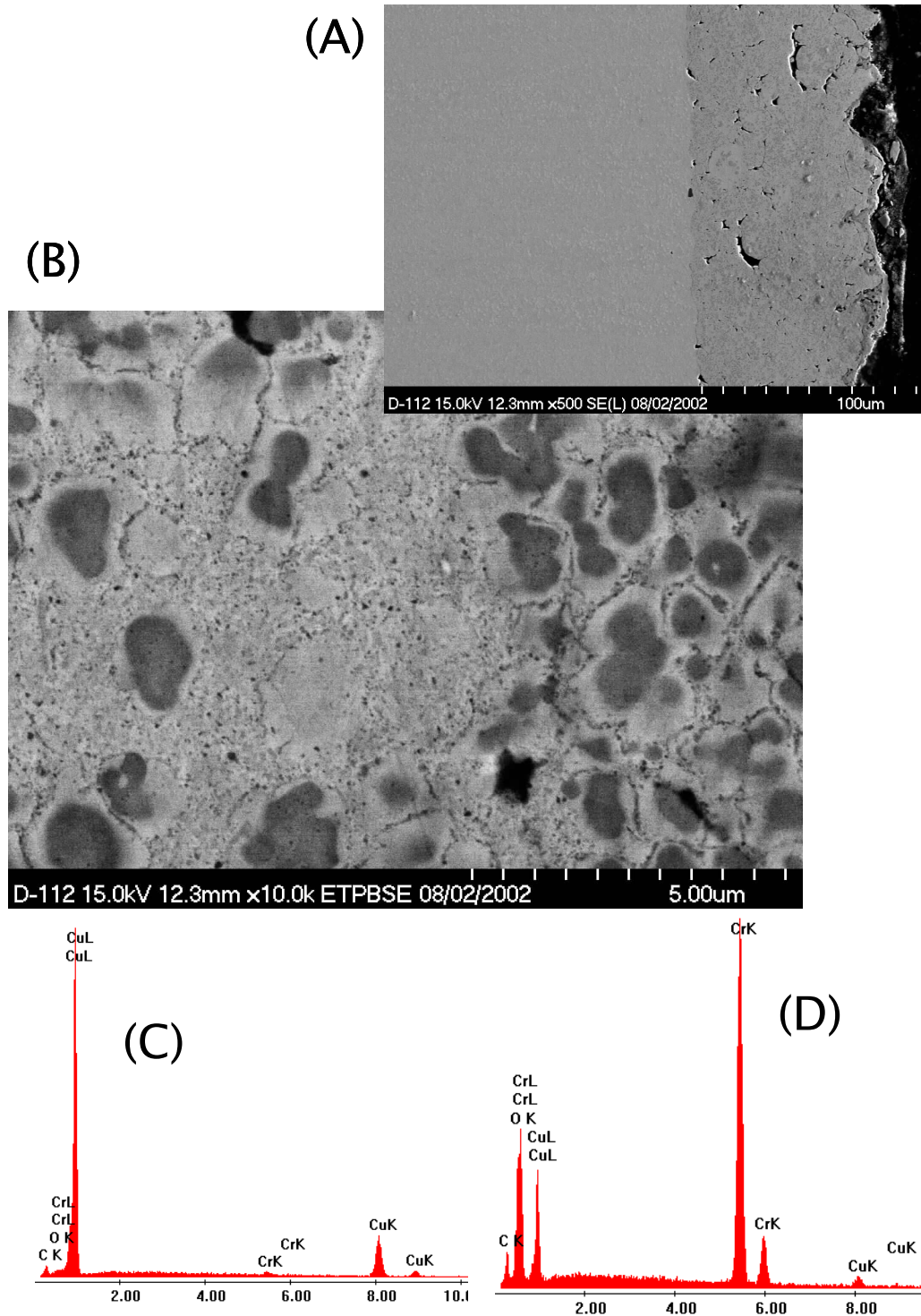


Fig. 1. SEM section of Cu₈Cr₄Nb, left in (A), coated with Cu-25.6%Cr and oxidized 10 hr at 650 °C. Higher magnification (B) reveals coating texture; EDS spectra (C), (D) identify Cu (light) and Cr (dark) phases.

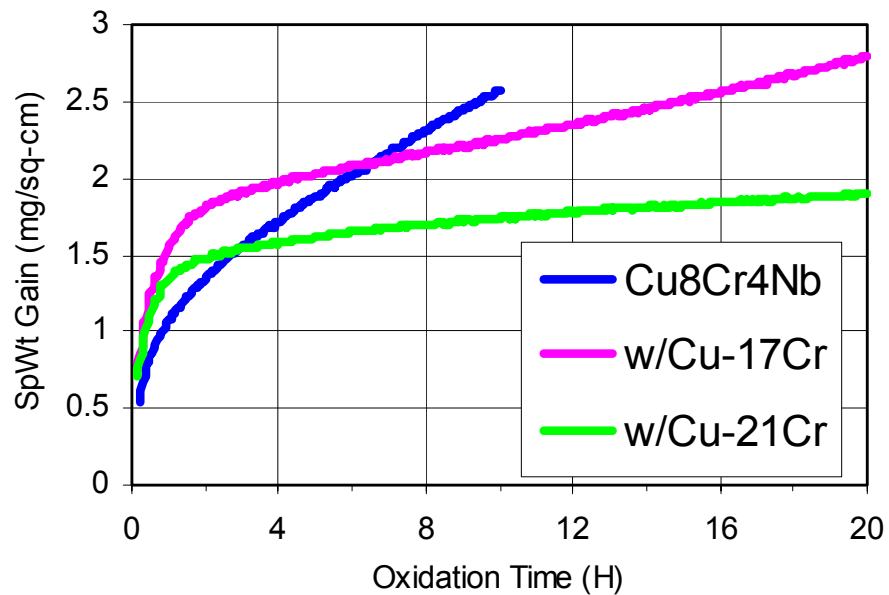
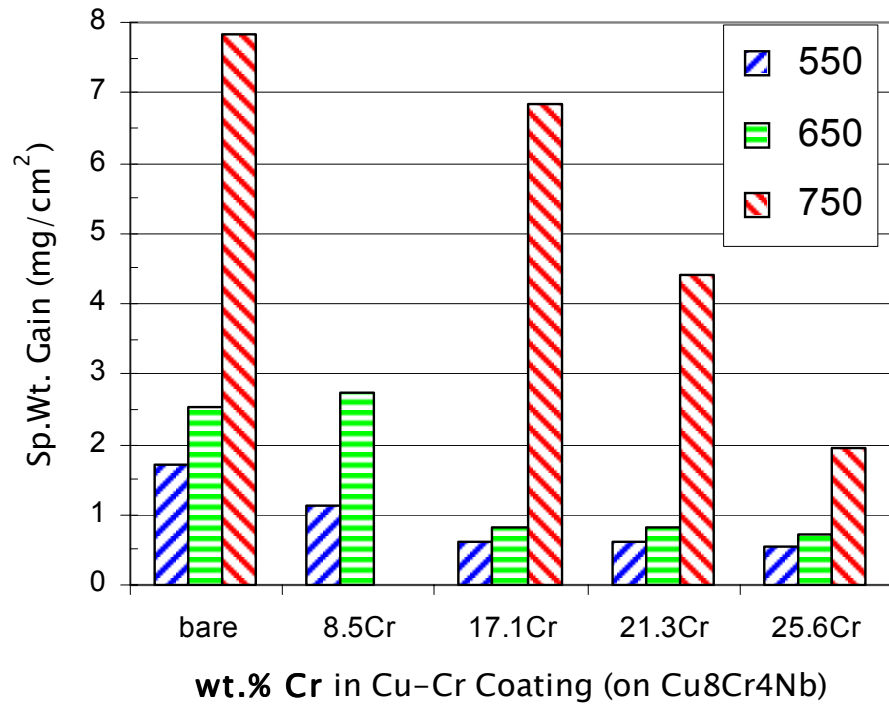


Fig. 2. (a) Static oxidation weight gains (at top), and (b) kinetics (bottom) at 650 °C, for Cu8Cr4Nb with and without Cu-Cr coatings.

The histograms illustrate two key facts. The first is that the coating reduces oxidation weight gain, by up to a factor of 4 compared with the uncoated alloy; indeed, the kinetic plots below the histograms illustrate the large differences in oxidation rates (i.e., in slopes) between the bare and coated alloy. The second is that the greater the Cr content of the coating, the more effective it was in reducing weight gain. A third fact, perhaps more interesting than the first two, is evident in the kinetic plot: For the coated samples, up to 80% of the net weight gain was registered in the

first ~1.5 hr, when parabolic kinetics associated with protective Cr_2O_3 had not been established. Figure 1(b) also shows that after 1 hr the coated sample has gained 30% more weight than the uncoated substrate: Oxidation weight gains in the pre-parabolic stage were consistently **higher** for the coated samples than for the bare alloy, a result that is contra-intuitive.

This seeming anomaly is explained by a point made earlier. The Cr_2O_3 layer starts as discrete nuclei, hence a coarse distribution of Cr will result in a coarse distribution of nuclei. Only when these nuclei coalesce into a continuous Cr_2O_3 layer does it become a protective diffusion barrier. Up to that point, oxidation of Cu in the coating proceeds unabated. Hence, the early-stage oxidation produces by far the most weight gain because it is strongly influenced by coating texture. While post-deposition heat treatment may consolidate the coating in the sense of improving particle adhesion and cohesion, it is unlikely to alter the texture. Coating texture is ultimately determined by the size of particle aggregates or “splats” that strike the substrate during deposition. This size factor may be improved by going to finer powders; however, the handling and delivery of very fine powders are not easy tasks. Apart from the coating texture, there may be inhomogeneity in the Cu-Cr distribution carried over from the powder; this is evident in Fig. 1. These inhomogeneities in coating textural and compositional determine when a continuous Cr_2O_3 layer begins to grow and oxidation protection becomes established.

Figure 2(a) shows also that above ~8%Cr and at temperatures below 750 °C, coating composition did not significantly affect sample weight gain. The reason for this is evident in Figs. 3 and 4. Figure 3 is from Cu-8.5Cr coating on a sample after oxidation at 650 °C. (Inset is a low-magnification image that includes the alloy substrate as well.) This figure shows a

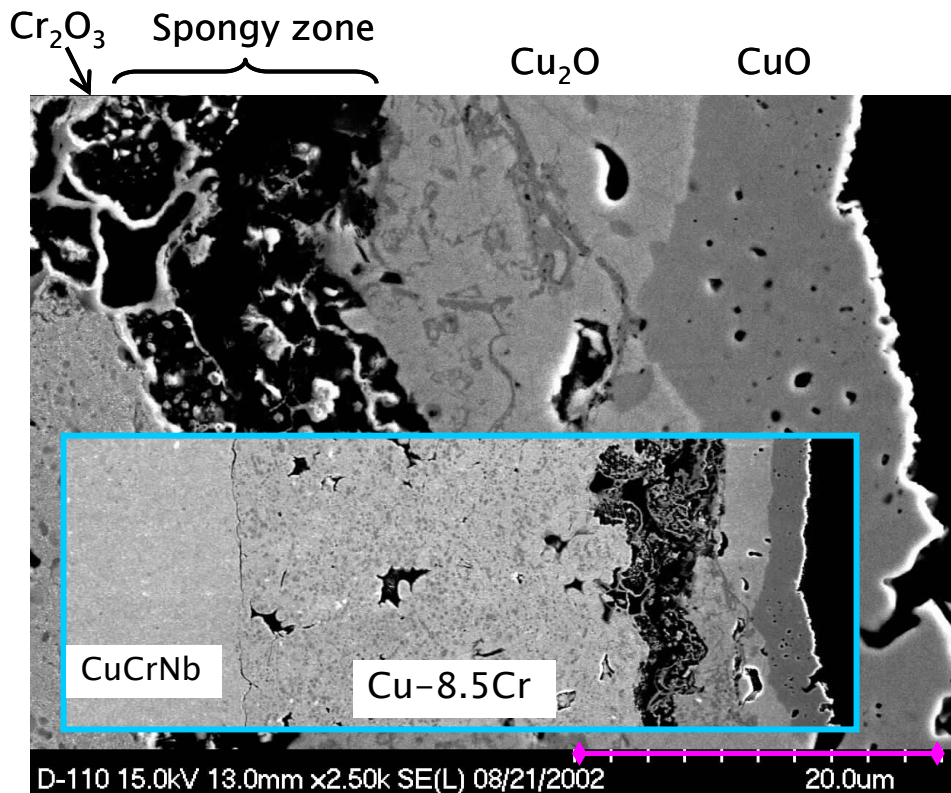


Fig. 3. SEM section of Cu8Cr4Nb coated with Cu-8.5%Cr, oxidized 10h at 650 °C, showing nascent Cr_2O_3 layer beneath copper oxides.

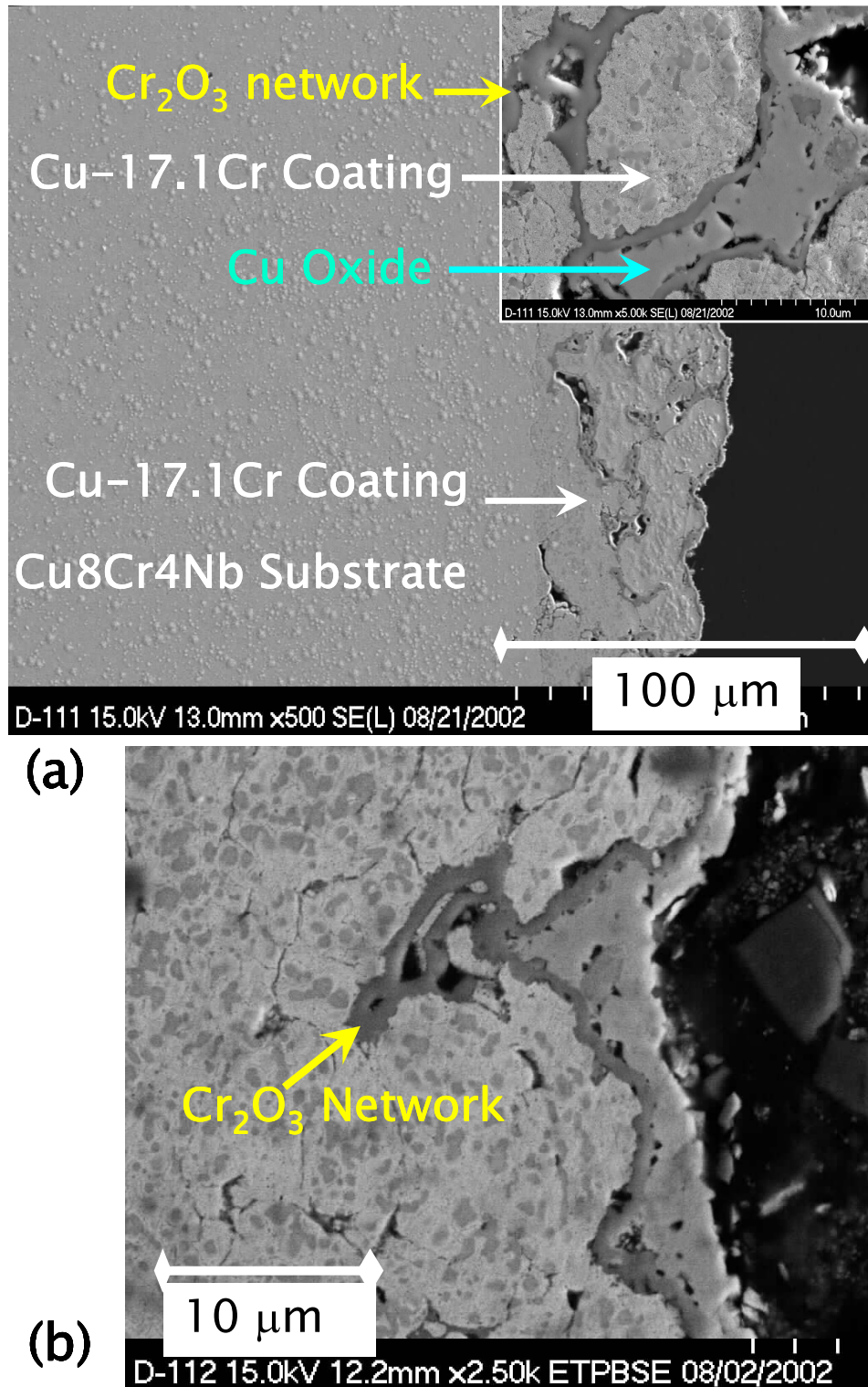


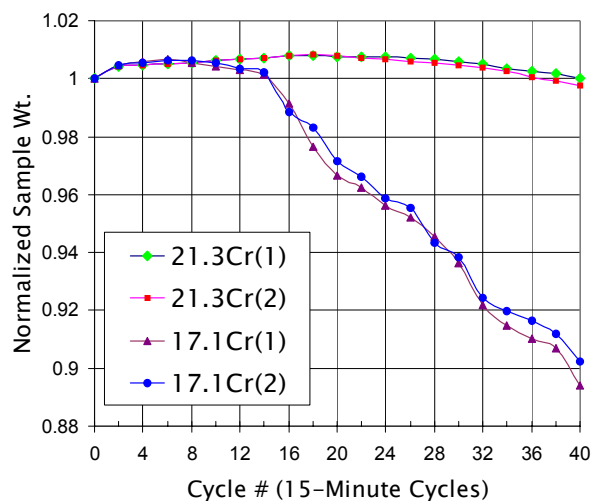
Fig. 4. SEM section of Cu-8Cr-4Nb coated with (a) Cu-17.1Cr and (b) Cu-25.6Cr and oxidized 10 hr at 650 °C. Note Cr₂O₃ networks.

filamentous early network of Cr_2O_3 just above the alloy substrate, separated from the copper oxide layers by a zone of friable material. (By analogy to similar features found in oxidized Cu-8Cr-4Nb [1,2], this zone is thought to be highly porous Cu_2O .) Figure 4 shows the same alloy coated with Cu-17.1Cr (a), and Cu-25.6Cr (b), and oxidized at 650 °C. A robust and continuous Cr_2O_3 layer is evident in both images. Thus, from the standpoint of Cr_2O_3 protection, there is no obvious advantage in Cr contents above ~17%. The question of whether the Cr reservoir in a Cu-17.1Cr coating is enough to sustain Cr_2O_3 growth is really a matter of the service life desired. For a space launch thruster, 10 hr of cumulative service (which represents hundreds of missions) is quite a long life.

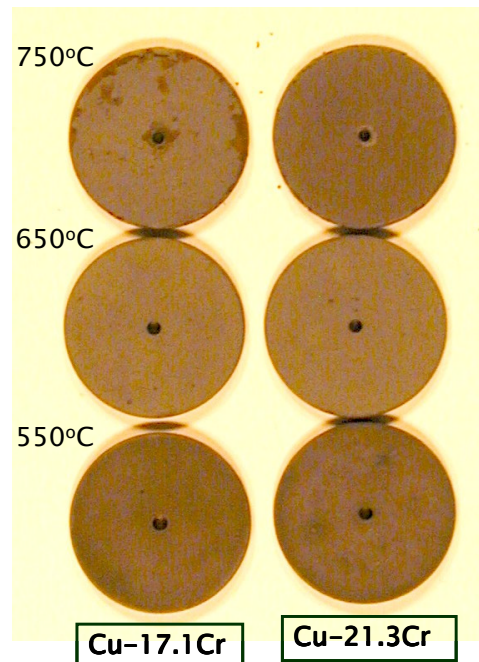
Cyclic Oxidation

Oxide films on these coatings and on the Cu-Cr-Nb substrate tended to spall off upon cooling; hence, resistance to cyclic oxidation is considered an important metric of performance, especially if a substantial thickness of oxide can build up during service. Cyclic oxidation results for Cu-17.1Cr and Cu-21.3Cr coatings on Cu8Cr4Nb are illustrated in Fig. 5.

Figure 5(a) is a chart of weight gains at 750 °C; the numbers in parentheses within the legend refer to repeat experiments. The Cu-21.3%Cr coating did not show any weight loss at 750 °C; hence there was no necessity to explore higher-Cr coatings. The Cu-17.1Cr coating began losing weight after ~3.5h at 750 °C; after 10 hr it was down to 90% of its starting weight. At 650 °C and below, none of the coatings registered any weight loss. In a separate experiment [7] the substrate alloy, Cu-8Cr-4Nb, was found to have lost 15% of its initial weight after similar oxidation cycles at 650 °C; and other Cu alloys were found to have lost significantly more weight. Hence, the effectiveness of these Cu-Cr coatings in protecting against cyclic-oxidation degradation is obvious.



(a)



(b)

Fig. 5. Cyclic-oxidation results for Cu-17.1Cr and Cu-25.5Cr.

Figure 5(b) shows the surface appearance of the samples after 40 oxidation cycles at various temperatures. The only visible degradation appeared on the Cu-17.1Cr coating after exposure at 750 °C. The oxide cover became breached around the edge and center hole, no doubt causing weight loss to begin in the 4th hour (Fig. 5(a)). Since temperatures at the wall are not expected to exceed 700 °C in service, the 750 °C results may be seen as approximating a worst-case cyclic-oxidation scenario.

Oxidation-Reduction Cycling

This aspect of the study was intended to determine how Cu-Cr coatings might fare in an environment in which Cu alloys are usually degraded by “blanching” (which is elaborated elsewhere [1,2] and in the companion paper [7]). Behavior in a cyclic oxidation-reduction test was considered an indicator of blanching resistance. The controls in this study were the alloys 3Ag-0.5Zr and Cu-8Cr-4Nb. The former exhibits no net change of weight in oxidation-reduction cycling and emerges with deep surface pits and fissures similar to features seen on this alloy after blanching attack in service; the latter registers a monotonic weight gain due to the growth of a protective oxide cover that resists reduction [7].

Figure 6 summarizes the results of oxidation-reduction cycling for Cu-Cr. Figure 6(a) plots weight change versus time for the three Cu-Cr coatings in the legend; all three behaved very similarly. Figure 6(b) is a high-resolution segment of the Cu-21.3Cr plot, showing individual weight gain-and-loss (oxidation-reduction) cycles. Figure 6(c) is a plot of weight gain versus square root of time, for the same Cu-21.3Cr, indicating overall parabolic weight gain, as may be expected for Cr_2O_3 protection. Figure 6(d) is an SEM image of the Cu-21.3Cr sample at the end

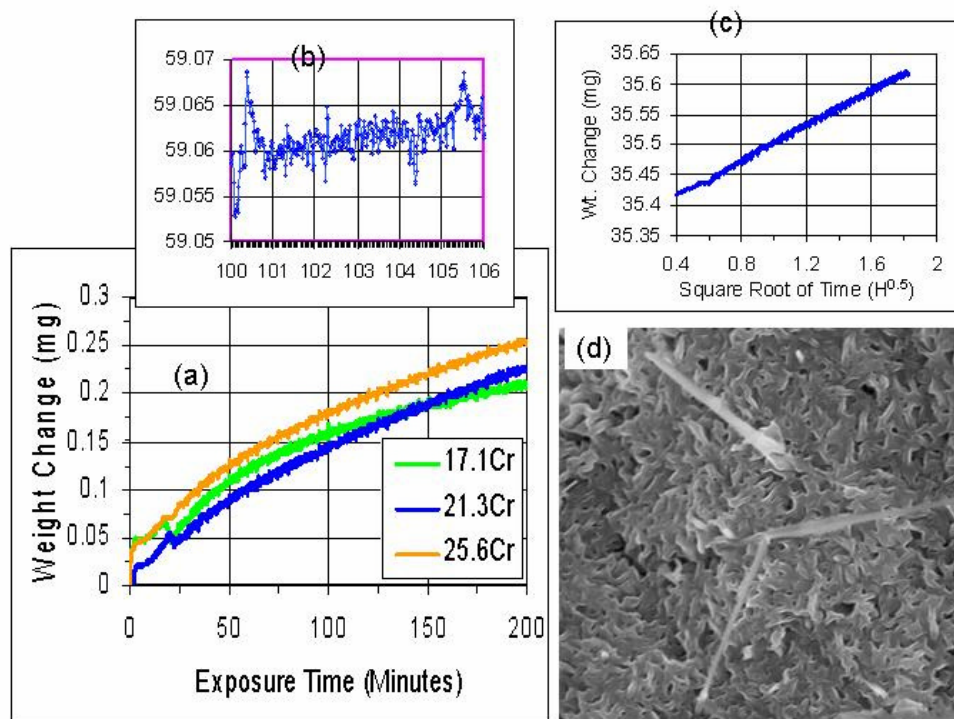


Fig. 6. Charts and image showing that oxidation-reduction cycling caused parabolic growth of Cr_2O_3 (only) on Cu-Cr coatings at 800 °C.

of cycling, showing a covering mat of oxide which was identified by EDS as Cr_2O_3 . Cu-17.1Cr and Cu-25.6Cr gave the same results: The $\text{Cu}_2\text{O}/\text{CuO}$ that formed during oxidation was completely removed by reduction in each cycle, leaving only Cr_2O_3 .

Note, however, that this result was obtained at 800 °C. It is not known what would happen at lower temperatures (say, 600 °C), where the growth of Cr_2O_3 is quite sluggish, while the growth of more easily reduced copper oxides is comparably brisk. This point is under investigation.

Summary and Conclusion

To assess their effectiveness as environmental barriers for Cu alloys, Cu-Cr coatings were tested for resistance to three categories of oxidation-related degradation: (1) static oxidation in 2.2% O_2 , (2) cyclic oxidation in air, and (3) oxidation-reduction cycling (in air and 5% H_2 environments). Cu-17.1Cr was found to be borderline adequate, whereas Cu-21.3Cr and Cu-25.5Cr were superior. But since Cu-21.3Cr and Cu-25.5Cr showed about the same level of resistance to degradation in all categories, there would be no need to go above 21.3%Cr content, in view of the attendant deficit in coating ductility and thermal conductivity. Further improvement may come from refining the coating texture and also homogenizing its composition. Using finer (<10-micron) powders and co-deposition of elemental Cu and Cr rather than pre-blended Cu-Cr powders are two ways to go. These approaches will be explored in future work.

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